Investigation of Photocatalytic Activity of Anatase Titanium Dioxide Prepared by DC Reactive Magnetron Sputtering for Air Pollutants Degradation

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In the present work, Titanium dioxide nanostructure were prepared by dc closed-field unbalanced reactive magnetron sputtering system using different values of Ar:O_2 gas mixing ratios. The magnetron sputtering system's operation parameters were optimized to prepare TiO_2 nanostructures as thin films with optical and structural homogeneity. The X-ray diffraction patterns and UV-visible spectroscopy show that the prepared films contain an anatase structure and an optical energy band gap of 3.2 eV. The production of Ti–O bonds has been confirmed by Fourier-transform infrared spectroscopy. The TiO_2 particles in the deposited films had an average size of 47.44 nm. TiO_2 as active photocatalyst material is employed in the field of air purification through using methane gas as an organic pollutant. The material's photocatalytic activity was evaluated by test the deterioration of polluted gas in the presence of a xenon lamp using an appropriate gas sensor (MQ2 gas sensor).

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1. Introduction

One of the world's problems is air pollution. It harms the environment and human health. Reducing these pollutants requires practical treatment methods and efficient technologies [1]. Photocatalytic oxidation is considered an ideal air purification technology because it can use sunlight (or artificial light) under ambient conditions to breakdown various air pollutants into non-toxic or less harmful forms [2]. A photocatalytic pollution treatment method was discovered using nano-TiO_2 materials [3,4]. After Honda and Fujishima discovered light-induced water decomposition on TiO_2 electrodes [5], the photocatalytic process began to be widely studied, especially for air and water polluted treatment. These studies focus on the photocatalytic activity of TiO_2 nanoparticles under ultraviolet (UV) light (λ<387nm), which accounts for only a small fraction (3-5%) of solar radiation [6]. Titanium dioxide (TiO_2) nanoparticles have got significant interest because of their distinct characteristics. Given its exceptional characteristics like non-toxicity, high photocatalytic activity, chemical stability, and suitability for use as a coating, photocatalytic properties offer a promising solution to address the existing issues with indoor air quality and building air purification systems [7-11]. A TiO_2 thin film deposited on a substrate is environmentally friendly and known as the most promising photocatalyst among all semiconductor photocatalysts [12,13]. The photocatalytic activity is related to the average nanocrystalline size, specific surface area of pure TiO_2, phases involved and crystallinity [14-19]. TiO_2 appears in three different polymorphs: anatase, rutile, and brookite. Anatase TiO_2 is the most active form of TiO_2 than rutile, and rutile is the most stable primary form [20-23]. TiO_2 can be prepared using a variety of deposition techniques including pulsed laser deposition (PLD), sputtering, sol-gel process, spray pyrolysis, chemical vapor deposition (CVD), electrophoretic deposition, etc. [24-27]. These nanoparticles were prepared using the magnetron sputtering technique to ensure high homogeneity, purity, and control over the structural phase of the deposited film by controlling the gas mixing ratio [28-31].

2. Experimental Part

In this work, nanostructured titanium dioxide films were deposited on glass substrates using dc reactive magnetron sputtering. The optimum operation and preparation conditions were selected to be discharge voltage of 3 kV, discharge current of 50 mA, the inter-electrode distance of 4 cm, Ar:O_2 gas mixing ratio of 50:50, and deposition time of 3 hours. More details on the sputtering system and optimum operation conditions can be found elsewhere [32-35]. The structural characteristics of the prepared samples were carried out on the nanopowders extracted from the thin film samples in order to avoid the contribution of the glass substrate on which the thin film was deposited. These nanopowders were extracted by the conjunctional freezing-assisted ultrasonic extraction method [36,37].

The system used to evaluate the effectiveness of gas purification consists of a cylindrical chamber with a diameter of 6 cm and a length of 30 cm. There is a gas injection port in this chamber. The xenon lamp inside the chamber is arranged along its length with its axis parallel to the cylinder's axis as shown in Fig. (1). The xenon lamp is operated with 6 W power and generates light spectrum centered at 300 nm. The chamber includes a MQ2 sensor. The interior wall of the cylinder is covered with glass slides on which the TiO_2 films were deposited. These slides cover an area of about 200 cm^2 in total. The deposited slides were placed three centimeters away from the xenon lamp. The gas concentration in parts per million (ppm) is displayed on a display screen via an Arduino card that has been pre-programmed and attached to the sensor. The displayed concentration is calibrated based on the type of gas being analyzed. This entire system is connected to a personal computer for real-time data recording during the examination, as depicted in Fig. (1). The gas concentration was continually measured and recorded within the closed chamber at one-second intervals during this test. The gas testing process included pumping the test gas into the chamber at a constant rate. In the first test, measurements were taken without injecting the gas. In the second test, gas pumping occurred without the use of the xenon lamp. In the third test, we introduced the xenon lamp while the pollutant gas was present to evaluate the photocatalytic effect on the tested gases inside the chamber. All recorded data was saved on the computer for subsequent analysis.

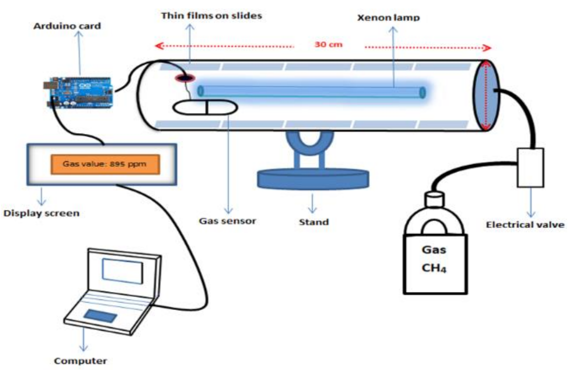


Fig. (1) Schematic diagram of the experimental system used for testing photocatalytic activity in air pollutants degradation

3. Results and Discussion

The structural characteristics bonds of TiO_2 films were determined through FTIR measurement using Shimadzu 8400S FTIR equipment. The Ti-O stretching vibration band appeared at approximately 447 and 667 cm^{-1}, and the Ti-O-Ti bonds in the TiO_2 lattice are responsible for the peak at 408.91 cm^{-1} [20, 21]. There are no peaks belonging to pollutions or contaminants, therefore, the samples can be categorized as highly pure. The absorption bands at approximately 3450 and 1620 cm^{-1} are caused by the stretching and bending vibrations, respectively, of the OH group in atmospheric water molecules [38-40].

The crystal structure of titanium dioxide samples was examined using a Shimadzu x-ray diffractometer using a Cu-K source (1.54Å). Figure (3) illustrates the XRD pattern of a TiO_2 thin film sample that was synthesized with a 50:50 gas mixing ratio and deposited time of three hours employing a heat sink under the substrate. This sample was selected as the optimum one among all others. According to JCPDS card no. 21-1272 (anatase TiO_2), nine different peaks may be seen in this figure, all of which are allocated to the anatase crystalline phase of TiO_2. In order to produce such nanostructures with highly-pure structural phases, dc reactive magnetron sputtering is advantageous, as demonstrated by the results, which exhibited no peaks belonging to the rutile phase in the synthesized sample.

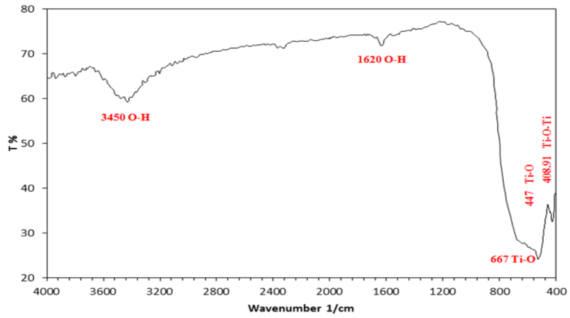


Fig. (2) FTIR spectrum of TiO_2 sample prepared at inter-electrode distance of 4 cm and using Ar:O_2 gas mixture of 50:50 after deposition time of 3 hours

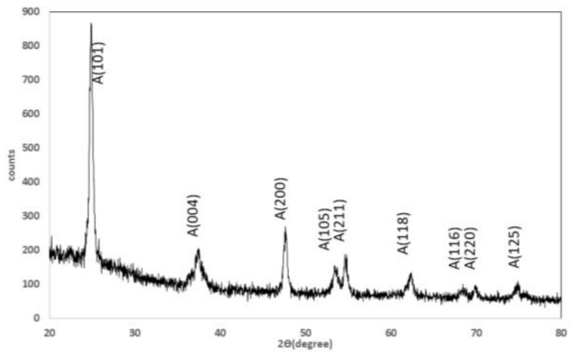


Fig. (3) XRD pattern for single-phase (anatase) TiO_2 sample prepared using gas mixing ratio of 50:50 after deposition time of 3 hours with heat sink under the substrate

The UV-visible spectroscopy was used to record and investigate the absorption spectra of TiO_2 film samples in the spectral region 300-800 nm using different gas mixing ratios as shown in Fig. (4). They exhibit considerable absorption to wavelengths shorter than 300 nm, peaking at approximately 312 nm. At 400 nm, the absorbance reaches its minimum and then rapidly decreases before gradually increasing at longer wavelengths. In the visible wavelength range of 400-700 nm, these films can be regarded as transparent. Consequently, the energy band gap of these samples can be determined using the following formula:

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \qquad (1)$$

where n is dependent on the type of transitions, A is a constant, and E_g is the optical energy band gap

The particle size of the prepared samples was ascertained using the FE-SEM. Figure (6) shows the image of the optimum TiO_2 sample, in which the nanoparticles are seen in irregular shapes and sizes and with average particle size of 47.44 nm. These particles aggregate and indicate good connectivity as they are held together by weak forces arising from the van der Waals force which leads to an electrostatic effects through the residual charge of the structure [41,42].

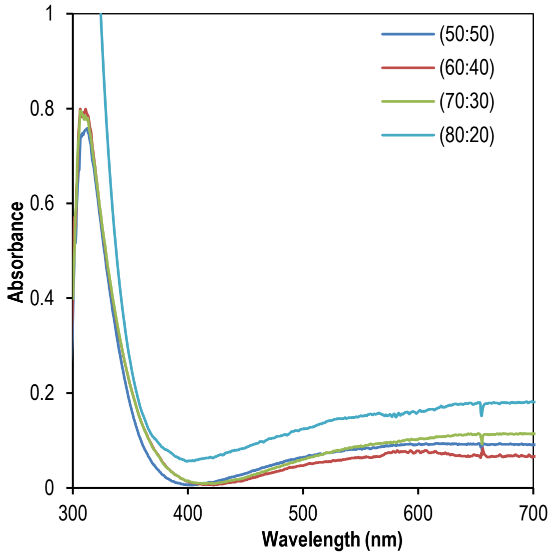
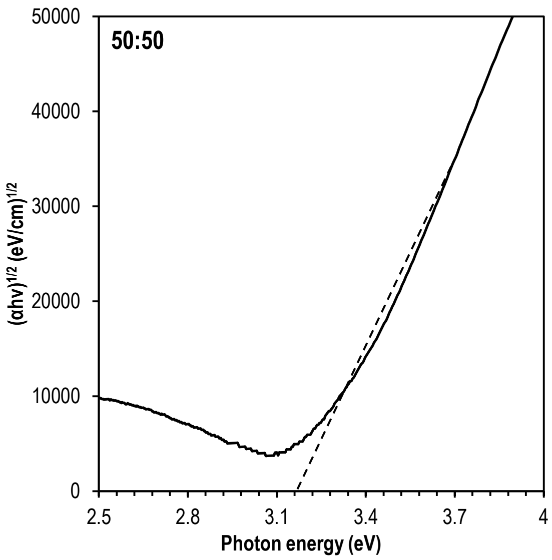
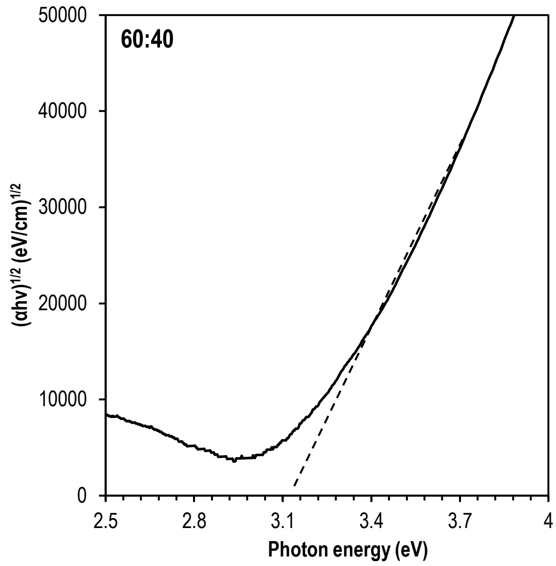


Fig. (4) Absorption spectra of TiO_2 thin films prepared using different Ar:O_2 gas mixing ratios

Figure (5) shows the determination of energy band gap for titanium dioxide thin films prepared using gas mixing ratios of (80:20), (70:30), (60:40) and (50:50) to be 3.24, 3.17, 3.16 and 3.2 eV, respectively. The optimum gas mixing ratio was (50:50) and thus energy band gap was determined to be 3.2 eV for single phase of anatase TiO_2.



(a)



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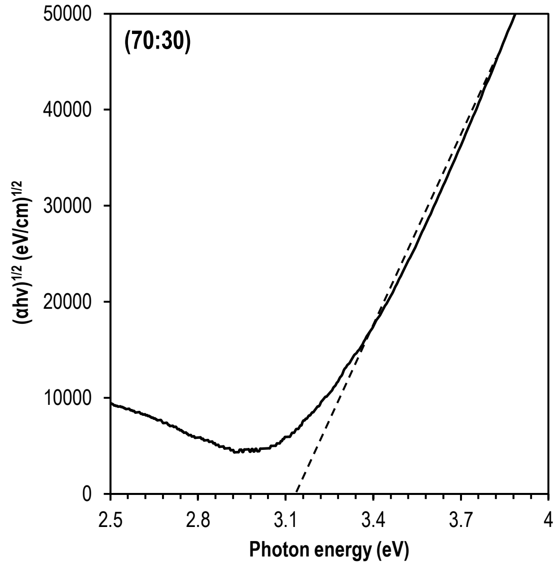

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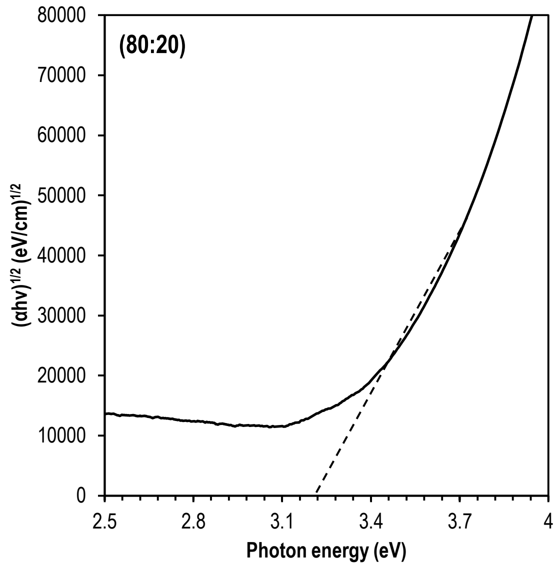


(d)

Fig. (5) Determination of energy band gap (E_g) for TiO_2 thin films prepared using different Ar:O_2 gas mixing ratios

The energy-dispersive x-ray (EDX) spectrum of the optimum sample was recorded and analyzed as shown in Fig. (7). This spectrum revealed the presence of titanium and oxygen in the thin layers and thus the formation of TiO_2 thin films was confirmed. With Ti and O present in the final sample, the weight ratios of Ti and O were 72.1% and 24.7%, respectively. The presence of 3.2% carbon is resulted from fixing the sample inside the EDX instrument.

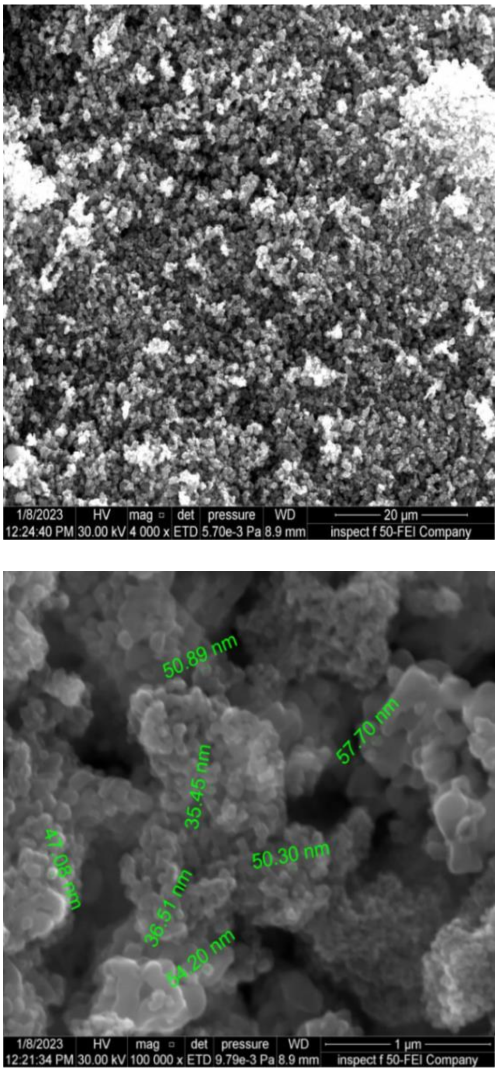
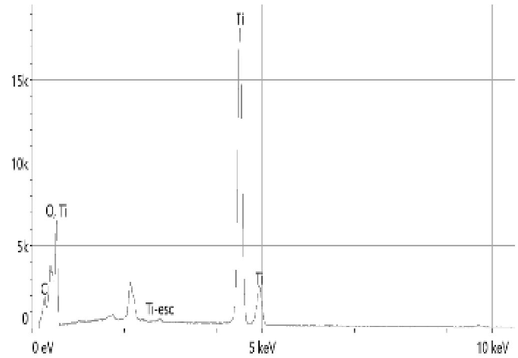


Fig. (6) FE-SEM images of the nanostructured anatase TiO_2 sample prepared using Ar:O_2 gas mixing ratio of 50:50, inter-electrode distance of 4 cm, and deposition time of 3 hours

The prepared nanostructured titanium dioxide thin films prepared were evaluated for their effectiveness in degradation of methane gas, which is a flammable, non-toxic, colorless, tasteless, and odorless gas. We measured the change in gas concentration over time in a sealed chamber containing static air, both before and after methane gas was added. The interaction between the gas and thin film deposited on glass substrate was monitored with and without the use of a xenon lamp. Initially, a steady gas concentration of 20 ppm was recorded in the static air representing the normal level of organic gases before adding methane. Upon pumping methane gas into the chamber and the xenon lamp was off, the gas concentration stayed mostly stable at approximately 898 ppm. On the other hand, the gas concentration progressively decreased upon switching the xenon lamp on and reached an almost constant value of 130 ppm over time period of 34 minutes as shown in Fig. (8).



Element	Atomic %	Weight %
C	8.0	3.2
O	46.6	24.7
Ti	45.4	72.1

Fig. (7) EDX results for the nanostructured anatase TiO_2 sample prepared using Ar:O_2 gas mixing ratio of 50:50, inter-electrode distance of 4 cm, and deposition time of 3 hours

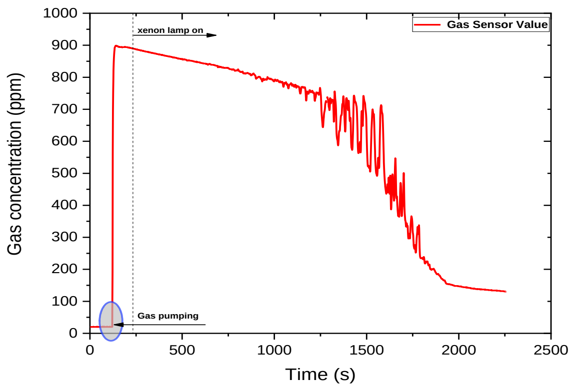


Fig. (8) Air purification test against methane gas based on photocatalytic effect of TiO_2 thin films prepared by dc reactive magnetron sputtering

4. Conclusion

In this study, nanostructured TiO_2 thin films – known as the optimum photocatalyst – were prepared by dc reactive magnetron sputtering technique and the energy band gap of these samples was determined to be 3.2eV, which belongs to the anatase phase of TiO_2. The prepared thin films are described by their optical and structural homogeneity. The prepared samples were tested in the field of air purification when irradiated by a xenon lamp. The results showed the high effectiveness of the prepared samples in air purification within a period of 34 min.

References

[1] F. He, W. Jeon and W. Choi, "Photocatalytic air purification mimicking the self-cleaning process of the atmosphere", *Nat. Commun.*, 12 (2021) 2528.

[2] B.S. Weon, F. He and W. Choi, "Status and challenges in photocatalytic nanotechnology for cleaning air polluted with volatile organic compounds: visible light utilization and catalyst deactivation", *Environ. Sci. Nano*, 6 (2019) 3185-3214.

[3] M.R. Hoffmann et al., "Environmental Applications of Semiconductor Photocatalysis", *Chem. Rev.*, 95(1) (1995) 69-96.

[4] A. Fujishima, T.N. Rao and D.A. Tryk, "Titanium dioxide photocatalysis", *J. Photochem. Photobio. C: Photochem. Rev.*, 1(1) (2000) 1-21.

[5] A. Fujishima and K. Honda, "Electrochemical Photolysis of Water at a Semiconductor Electrode", *Nature*, 238 (1972) 37-38.

[6] T. Tachikawa, M. Fujitsuka and T. Majima, "Mechanistic Insight into the TiO_2 Photocatalytic Reactions: Design of New Photocatalysts", *J. Phys. Chem. C*, 111(14) (2007) 5259-5275.

[7] N.H. Hashim, F.J. Kadhim and Z.S. Abdulsattar, "Characterization of Electrochromism and Photoelectrochromism of N-Doped TiO_2 and Co_3O_4 Thin Films Prepared by DC Reactive Magnetron Sputtering: Comparative Study", *Iraqi J. Appl. Phys.*, 19(1) (2023) 5-12.

[8] M.A. Nima and F.J. Kadhim, "Photocatalytic Performance of Mixed and Single Phases of Titanium Dioxide Nanoparticles on Growth of Fusarium Oxysporum Fungal", *Iraqi J. Appl. Phys.*, 17(4) (2021) 9-14.

[9] O.A. Hammadi et al., "Photocatalytic Activity of Nitrogen-Doped Titanium Dioxide Nanostructures Synthesized by DC Reactive Magnetron Sputtering Technique", *Nonl. Opt. Quantum Opt.*, 51(1-2) (2019) 67-78.

[10] E.A. Al-Oubidy and F.J. Al-Maliki, "Photocatalytic activity of anatase titanium dioxide nanostructures prepared by reactive magnetron sputtering technique", *Opt. Quantum Electron.*, 51(1-2) (2019) 23.

[11] Z.H. Zaidan et al., "Effect of Structural Phase on Photocatalytic Activity of Titanium Dioxide Nanoparticles", *Iraqi J. Appl. Phys.*, 19(3A) (2023) 55-58.

[12] E.A. Al-Oubidy and F.J. Al-Maliki, "Effect of Gas Mixing Ratio on Energy Band Gap of Mixed-Phase Titanium Dioxide Nanostructures Prepared by Reactive Magnetron Sputtering Technique", *Iraqi J. Appl. Phys.*, 14(4) (2018) 19-23.

[13] R.A.H. Hassan and F.T. Ibrahim, "Preparation and Characterization of Anatase Titanium Dioxide Nanostructures as Smart and Self-Cleaned Surfaces", *Iraqi J. Appl. Phys.*, 16(4) (2020) 13-18.

[14] K.V. Baiju et al., "Photocatalytic activity of Sol-Gel-Derived nanocrystalline Titania", *J. Phys. Chem. C*, 111(21) (2007) 7612-7622.

[15] M. Riazian, "Electrical properties, and enhancement of photocatalytic activity of TiO_2 nanorods doped with SiO_2", *S. Afr. J. Chem.*, 70 (2017) 189-199.

[16] E.A. Ajaj, Z.R. Musleem and B.M. Al-Shabander, "Preparation of TiO_2 nanorods by Sol-Gel template method and measured its photo-catalytic activity for degradation of methyl orange", *Iraqi J. Phys.*, 13(26) (2015) 171-177.

[17] S.S. Al-Awadi et al., "Optical and Structural Properties of Titanium Dioxide Papered by DC Magneton-Sputtering as a NO_2 Gas Sensor", *Iraqi J. Sci.*, 61(10) (2020) 2562-2569.

[18] F.J. Al-Maliki, O.A. Hammadi and E.A. Al-Oubidy, "Optimization of Rutile/Anatase Ratio in Titanium Dioxide Nanostructures prepared by DC Magnetron Sputtering Technique", *Iraqi J. Sci.*, 60 (2019) 91-98.

[19] F.J. Al-Maliki and E.A. Al-Oubidy, "Effect of gas mixing ratio on structural characteristics of titanium dioxide nanostructures synthesized by DC reactive magnetron sputtering", *Physica B: Cond. Matter*, 555 (2019) 18-20

[20] F.J. Al Maliki and M.A. Al Rubaiy, "Synthesis and study the concentration effect on the photocatalytic activity of titania nanoparticles as antibactria using reactive magnetron sputtering technique", *Opt. Quantum Electron.*, 54 (2022) 377.

[21] F.J. Kadhim, O.A. Hammadi and E.A. Al-Oubidy, "Optimization of Rutile/Anatase Ratio in Titanium Dioxide Nanostructures prepared by DC Magnetron Sputtering Technique", *Iraqi J. Sci.*, 60 (2019) 91-98.

[22] Z.H. Zaidan et al., "Using Banana Peels for Green Synthesis of Mixed-Phase Titanium Dioxide Nanopowders", *Iraqi J. Appl. Phys.*, 18(4) (2022) 27-30.

[23] D.M. Challoob, M.Y. Khdiar and O.A. Hammadi, "Highly-Pure Titanium Dioxide nanopowders Synthesized by EcoFriendly Solvothermal Method", *Iraqi J. Appl. Phys.*, 20(2B) (2024) 381-386.

[24] R. Hippler et al., "Deposition of cobalt oxide films by reactive pulsed magnetron sputtering", *Surf. Coat. Technol.*, 405 (2021) 126590.

[25] O.A. Hammadi and N.E. Naji, "Fabrication and Characterization of Polycrystalline Nickel Cobaltite Nanostructures Prepared by Plasma Sputtering as Gas Sensor", *Phot. Sen.*, 8(1) (2018) 43-47.

[26] R.O. Abdulsada and T.A.A. Hassan, "Synthesis of TiO_2 Thin Films Nanoparticles with Different

Layers using Simple Sol-Gel Method", *Iraqi J. Sci.*, 62(11) (2021) 4425-4429.

[27] M.B. Al-Taee and B.M. Alshabander, "Photocatalytic Degradation of Methyl blue by TiO_2 Nanoparticles Incorporated in Cement", *Iraqi J. Phys.*, 21(1) (2023) 10-20.

[28] N. H. Hashim, F. J. Kadhim, "Structural and Optical Characteristics of Co_3O_4 Nanostructures Prepared by DC Reactive Magnetron Sputtering", *Iraqi J. Appl. Phys.*, 18(4) (2022) 31-36.

[29] M.A. Hameed, S.H. Faisal, R.H. Turki, "Characterization of Multilayer Highly-Pure Metal Oxide Structures Prepared by DC Reactive Magnetron Sputtering Technique", *Iraqi J. Appl. Phys.*, 16(4) (2020) 25-30

[30] R.A.H. Hassan and F.T. Ibrahim, "Preparation and Characterization of Ni-doped TiO_2 Nanostructures for Surface Cleaning Applications", *Iraqi J. Appl. Phys.*, 17(1) (2021) 3-8.

[31] Z.H. Zaidan et al., "Effect of Preparation Method on Crystalline Structure of Titanium Dioxide Nanoparticles", *Iraqi J. Appl. Phys. Lett.*, 6(2) (2023) 11-14.

[32] O.A. Hammadi et al., "Operation Characteristics of a Closed-Field Unbalanced Dual-Magnetrons Plasma Sputtering System", *Bulg. J. Phys.*, 41(1) (2014) 24-33.

[33] O.A. Hammadi et al., "Employment of Magnetron to Enhance Langmuir Probe Characteristics of Argon Glow Discharge Plasma in Sputtering System", *Iraqi J. Appl. Phys.*, 12(4) (2016) 19-28.

[34] A.M. Hameed and M.A. Hameed, "Highly-Pure Nanostructured Metal Oxide Multilayer Structure Prepared by DC Reactive Magnetron Sputtering Technique", *Iraqi J. Appl. Phys.*, 18(4) (2022) 9-14.

[35] A.M. Hameed and M.A. Hameed, "Spectroscopic characteristics of highly pure metal oxide nanostructures prepared by DC reactive magnetron sputtering technique", *Emerg. Mater.*, 6 (2022) 627-633.

[36] O.A. Hammadi, "Production of Nanopowders from Physical Vapor Deposited Films on Nonmetallic Substrates by Conjunctional Freezing-Assisted Ultrasonic Extraction Method", *Proc. IMechE, Part N, J. Nanomater. Nanoeng. Nanosys.*, 232(4) (2018) 135-140.

[37] O.A. Hammadi, "Effects of Extraction Parameters on Particle Size of Titanium Dioxide Nanopowders Prepared by Physical Vapor Deposition Technique", *Plasmonics*, 15(6) (2020) 1747-1754.

[38] J. Mohan, "Organic spectroscopy principles and applications", 2nd ed., Narosha Publishing House Pvt. Ltd, New Delhi, 28–95, 2009.

[39] R.A. Aziz and I. Sopyan, "Synthesis of TiO_2-SiO_2 powder and thin film photocatalysts of sol-gel method", Int. J. Chem., Vol. 48, pp. 951-957, 2009

[40] F.J. Al-Maliki, O.A. Hammadi and N. Muthesher, "Photocatalytic activity of TiO_2/SiO_2 nanocomposites synthesized by reactive magnetron sputtering technique", *J. Nanophot.*, 16(2) (2022) 026005.

[41] F.J. Al-Maliki and N.H. Al-Lamey, "Synthesis of Tb-doped titanium dioxide nanostructures by sol–gel method for environmental photocatalysis applications", *J. Sol-Gel Sci. Technol.*, 81(1) (2017) 276-283.

[42] Y. Zhao et al., "Synthesis and optical properties of TiO_2 nanoparticles", *Mater. Lett.*, 61(1) (2007) 79-83.